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Reactions of 2-Arylthio- and 2-Arylsulfonyl-1-nitro-1-phenylethenes with Amines

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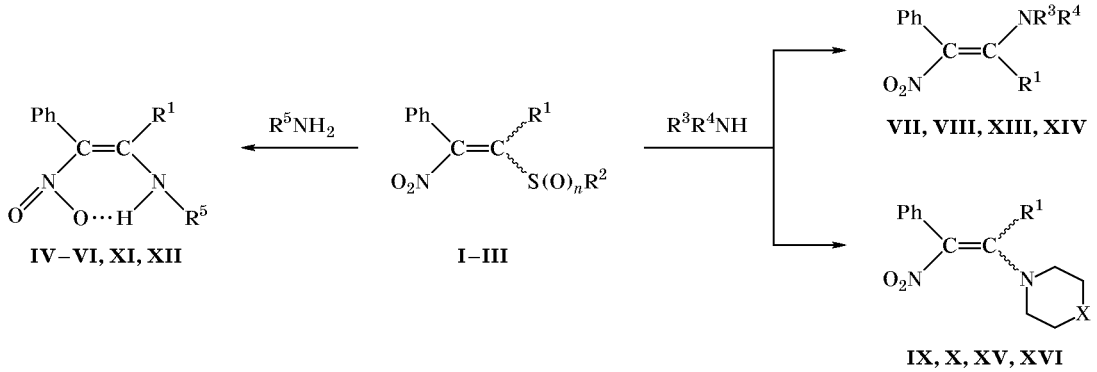
Abstract—2-Arylthio- and 2-arylsulfonyl-1-nitro-1-phenylethenes react with amines to give the corresponding nitroenamines whose configuration (*E* or *Z*) depends on the amine structure. Primary amines gives rise to *Z*-nitroenamines, secondary cyclic amines with 2-arylthio-1-nitroalkenes form *E*-nitroenamines, and with more reactive 2-arylsulfonyl-1-nitroalkenes *E*/*Z*-isomeric mixtures are obtained.

The presence of a readily departing group in the β-position with respect to the nitro group determines the high reactivity of 2-arylthio- and 2-arylsulfonyl-1-nitro-1-phenylethenes toward nucleophilic reagents and formation of the corresponding substitution products [1]. We previously described reactions of sulfur-containing nitroalkenes with alkoxide and thiolate ions [2, 3], as well as with some amines (e.g., aniline and morpholine [2]). In addition, reactions of R-thio-nitroalkenes with pyrrolidine [4] and three aliphatic amines [5] were reported. The products of these reactions were the corresponding nitroenamines; however, neither the reactivity of various R-thio- and R-sulfonyl-substituted substrates nor the relations between the product configuration and initial amine structure were examined.

With the goal of studying in more detail the reactivity of 1-nitro-2-R-thio(sulfonyl)ethenes toward various amines and revealing the relations between the amine nature and steric structure of the resulting nitroenamines, 2-(4-chlorophenylthio)-1-nitro-1-phenylethene (**I**) and 2-arylsulfonyl-1-nitro-1-phenylethenes **II** and **III** were brought into reactions with primary and secondary amines. The reactions with such aliphatic amines as diethylamine, dipentylamine, and benzylamine were carried out for the the first time. As secondary cyclic amines we used piperidine and morpholine. As a result, nitroenamines **IV**–**XVI** were obtained (Tables 1–3; Scheme 1).

As expected, ammonia and aliphatic amines (benzylamine, dialkylamines) reacted with compounds **I**–**III** more readily than did aromatic amines (aniline

Scheme 1.



I, R^1 = H, R^2 = 4-ClC_6H_4, *n* = 0; **II**, R^1 = H, R^2 = 4-$CH_3C_6H_4$, *n* = 2; **III**, R^1 = Ph, R^2 = 4-$CH_3C_6H_4$, *n* = 2; **IV**, R^1 = R^5 = H; **V**, R^1 = H, R^5 = $PhCH_2$; **VI**, R^1 = H, R^5 = 4-$NO_2C_6H_4$; **VII**, R^1 = H, R^3 = R^4 = Et; **VIII**, R^1 = H, R^3 = R^4 = C_5H_{11}; **IX**, R^1 = H, X = CH_2; **X**, R^1 = H, X = O; **XI**, R^1 = Ph, R^5 = H; **XII**, R^1 = Ph, R^5 = $PhCH_2$; **XIII**, R^1 = Ph, R^3 = R^4 = Et; **XIV**, R^1 = Ph, R^3 = R^4 = C_5H_{11}; **XV**, R^1 = Ph, X = CH_2; **XVI**, R^1 = Ph, X = O.

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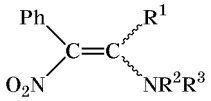
Table 1. Melting points and spectral parameters of 2-amino-1-nitroethenes **IV**–**XVI**



Comp. no.	mp, °C	Isomer	IR spectrum, ν, cm^{-1}		^1H NMR spectrum, δ, ppm				UV spectrum, λ_{max}, nm (ε, $l\ mol^{-1}\ cm^{-1}$)
			NOO^- (NO_2)	C=C, C=N	Ph	R^1	R^2	R^3	
IV	92–93	*Z*	1380, 1280, 1180	1640	7.11–7.27 m		9.00 br		245 [9500] 368 [12 000]
V	84–85	*Z*	1385, 1365, 1175	1640	7.45–7.50 m	7.14 s	9.69 br	4.59 d,[a] 7.45–7.50 m	262 [10 000] 368 [12 000]
VI	224–225	*Z*	1335, 1175, 1120	1650, 1630	7.19–7.69 m		11.10 br	7.19–7.69 m	
VII	67–69	*E*	1375, 1285	1620, 1595	7.30–7.42 m	8.50 s	1.09 t, 3.07 q		364 [16 000]
VIII	52–53	*E*	1380, 1275	1660, 1590	7.29–7.40 m	8.45 s	0.90 t, 1.25 q, 1.59 m, 3.15 q		
IX	135–136	*E*[b]	1385, 1265[c]	1625		8.47 s	1.52 s, 3.09 m		257 [9300]
	Oil	*Z*[d]	1170		7.26–7.38 m	7.85 s			368 [20 000]
X	160–161	*E*[b]	1370, 1170	1640, 1590		8.40 s	3.09, 3.19, 3.46,		410 [10 000]
	Oil	*Z*[d]			6.85–7.30 m	7.80 s	3.70 m		
XI	157–158	*Z*	1393, 1291	1600	7.10–7.28 m		10.00 br		240 [9200] 360 [12 000]
XII	160–161	*Z*	1375, 1180, 1135	1590, 1570	7.32 m	7.11 m	11.34 s	4.32 d, 7.00 m	257 [5200] 370 [13 500]
XIII	130–131	*Z*	1375, 1285, 1180	1595, 1580	7.26 m	7.15 m	1.15 t, 3.18 q		
XIV	69–70	*Z*	1375, 1240, 1180	1595, 1580	7.26 m	7.12 m	0.89 t, 1.23 q, 1.57 m, 3.12 t		262 [4200] 420 [4400]
XV	167–168	*Z*	1290, 1230, 1180	1595, 1590	7.31 m	7.11 m	1.68 s, 3.02 s		257 [12 000] 424 [10 500]
XVI	204–205	*Z*	1305, 1120	1600, 1570	7.10–7.20 m	6.95 m	2.55, 3.18, 3.81 m		257 [7700] 414 [7000]

[a] J = 10 Hz.
[b] From compound **I**.
[c] In KBr.
[d] From compound **II**.

and *p*-nitroaniline; Table 2). Arylsulfonyl-substituted compounds **II** and **III** turned out to be more reactive than **I**, and the styrene derivative was more reactive than stilbene **III** (Table 2). Styrene **I** and stilbene **III** failed to react with such a weak nucleophile as *p*-nitroaniline in boiling acetonitrile (24 h).

The structure of previously unknown 2-amino-1-nitroethenes was confirmed by spectral data (Table 1). Their IR spectra are typical of strongly polarized nitroenamine systems [6]: a strong "enamine" band is observed in the region 1660–1570 cm^{-1}, and stretching vibrations of the nitro group give rise to absorption at 1510–1440 cm^{-1} ($\nu_{as}N-O$, weak band) and 1300–1170 cm^{-1} ($\nu_s N-O$). The UV spectra contain a long-wave charge-transfer band at λ 340–410 nm.

The configuration of nitroenamines was determined on the basis of the ^1H NMR spectra. It is known that in the absence of deshielding effect of the nitro group (through space) the signal from the olefinic proton of the *Z* isomer appears in a stronger field relative to the corresponding signal of the *E* isomer [7]. The position of the β-vinyl proton signal in the spectra of secondary aminonitrostyrenes **IV**–**VI** (δ 7.14–7.80 ppm) suggests that their molecules have *Z* configuration. The structure of tertiary aminonitroalkenes depends on the amine nature. Compounds **VII** and

Table 2. Reaction of nitroalkenes **I**–**III** with amines; given are product no., configuration, reaction time, and yield

Comp. no.	Solvent	Ammonia[a]	Benzylamine	*p*-Nitroaniline[b]
I	Diethyl ether	**IV** (*Z*), 90 min, 34%	**V** (*Z*), 100 min, 60%	**I**, 4 h, 60°C, 95%
II	Diethyl ether	**IV** (*Z*), 5 min, 39%	**V** (*Z*), 25 min, 57%	**VI** (*Z*), 20 min,[c] 73%
III	Methanol Acetonitrile	**XI** (*Z*), 30 min, 20°C, 52%	**XII** (*Z*), 20 min, 50°C, 87%	**III**, 24 h, 60°C, 98%

Comp. no.	Solvent	Diethylamine	Dipentylamine	Piperidine	Morpholine
I	Diethyl ether	**VII** (*E*), 40 min, 41%	**VIII** (*E*), 40 min, 40%	**IX** (*E*), 45 min, 46%	**X** (*E*), 50 min, 75%
II	Diethyl ether	**VII** (*E*), 15 min, 30%	**VIII** (*E*), 15 min, 27%	**IX** (*E*/*Z*), 10 min, 57%	**X** (*E*/*Z*), 25 min, 70%
III	Methanol Acetonitrile	**XIII** (*Z*), 15 min, 50°C, 64%	**XIV** (*Z*), 15 min, 50°C, 43%	**XV** (*Z*), 5 min, 50°C, 82%	**XVI** (*Z*), 10 min, 50°C, 68%

[a] The reaction was carried out in $MeOH/H_2O$ at 18–20°C.

[b] The reaction with aniline in methanol at room temperature was complete in 3 h [2].

[c] The reaction was carried out in acetonitrile.

VIII derived from secondary aliphatic amines are *E* isomers; the chemical shifts of the olefinic protons therein are δ 8.50 and 8.45 ppm, respectively. Nitroenamines **IX** and **X** obtained from arylsulfonylalkene and cyclic amines were isolated as mixtures of *E* and *Z* isomers (Table 1), whereas the reaction with less reactive arylthioethene **I** gave only more stable *E* isomer.

According to the TLC and ^{1}H NMR data, nitroenamines **XI**–**XVI** of the stilbene series were isolated as single isomers. The *Z* configuration of **XI** and **XII** was assigned by analysis of the ^{1}H chemical shifts of both β-phenyl protons and proton on the amino nitrogen atom. Their signals are displaced downfield (δ 10.0 and 11.50 ppm, respectively) due to deshielding effect of the nitro group in the *cis*-position. Likewise, the NH proton signal in the spectra of *Z*-styrene derivatives **IV** and **V** is observed at δ > 9.00 ppm (Table 1), in keeping with published data for (*Z*)- and (*E*)-2-amino-1-nitroethenes: δ 9.00–11.50 ppm (*Z*) and δ < 9 ppm (*E*) [6–8]. This conclusion is supported by the upfield position of signals from the β-phenyl protons (δ 7.11 ppm) relative to those of the α-phenyl protons (δ 7.28 and 7.32 ppm). The assignment of tertiary nitroenamines **XIII**–**XVI** to the *Z* series is less reliable. It was made on the basis of the chemical shifts of the phenyl protons, which are similar to those observed for *Z* isomers **XI** and **XII**. According to the data of [9], 1-nitro-2-piperidino-1,2-diphenylethene has also *Z* configuration.

The reaction of 2-arylthio- and 2-arylsulfonyl-1-nitroethenes with alkylamines may be regarded as a preparative route to 2-alkylamino-1-nitroethenes, taking into account that the other β-functionalized nitroalkenes are less accessible and that their reactions with strongly basic aliphatic amines are accompanied by considerable tarring.

EXPERIMENTAL

The IR spectra were recorded on a Specord-75IR spectrometer in chloroform (unless otherwise stated). The ^{1}H NMR spectra were obtained on a Tesla BS-487C instrument (80 MHz) in $CDCl_3$. The UV spectra were measured on a Specord M-40 spectrophotometer. The progress of reactions was monitored, and the purity of products was checked, by TLC on Silufol UV-254 plates using hexane–acetone (2:1) as eluent. Some products were isolated and purified by column chromatography on silica gel (L 100/250 μm, Czechia); eluents were selected according to the Trappe series. 2-(4-Chlorophenylthio)-1-nitro-1-phenylethene (**I**) [10], 1-nitro-1-phenyl-2-(4-tolylsulfonyl)ethene (**II**), and 1-nitro-1,2-diphenyl-2-(4-tolylsulfonyl)ethene (**III**) [11] were synthesized by known methods.

Table 3. Elemental analyses of aminonitroethenes **IV**–**XVI**

Compound no.	Found, %			Formula	Calculated, %		
	C	H	N		C	H	N
IV	58.49	4.83	17.18	$C_8H_8N_2O_2$	58.54	4.88	17.07
V	70.79	5.61	11.05	$C_{15}H_{14}N_2O_2$	70.87	5.52	11.02
VI	59.07	3.91	14.68	$C_{14}H_{11}N_3O_4$	58.94	3.85	14.73
VII	65.39	7.33	12.80	$C_{12}H_{16}N_2O_2$	65.45	7.27	12.73
VIII	69.98	13.78	13.70	$C_{18}H_{28}N_2O_2$	71.05	13.79	13.79
IX	67.33	6.71	12.13	$C_{13}H_{16}N_2O_2$	67.24	6.89	12.07
X	57.99	5.53	17.00	$C_{12}H_{14}N_2O_3$	58.06	5.65	16.94
XI	70.01	4.95	11.58	$C_{14}H_{12}N_2O_2$	70.00	5.00	11.67
XII	76.08	5.61	8.46	$C_{21}H_{18}N_2O_2$	76.36	5.46	8.49
XIII	72.83	6.91	9.38	$C_{18}H_{20}N_2O_2$	72.97	6.76	9.46
XIV	75.40	8.69	7.59	$C_{24}H_{32}N_2O_2$	75.79	8.42	7.37
XV	74.20	6.62	9.08	$C_{13}H_{30}N_2O_2$	74.03	6.49	9.09
XVI	61.98	12.09	11.98	$C_{12}H_{28}N_2O_3$	62.07	12.07	12.07

(*Z*)-2-Amino-1-nitro-1-phenylethene (IV). To a solution of 0.30 g (1 mmol) of 1-nitro-1-phenyl-2-(4-tolylsulfonyl)ethene (**II**) in 10 ml of methanol we added dropwise 2 ml (1 mmol) of 25% aqueous ammonia. The mixture instantaneously turned bright creamson, and 5 min after it became lemon yellow. The solvent was distilled off on a rotary evaporator, and the residue was subjected to column chromatography on silica gel. By elution with chloroform we isolated 0.064 g of nitroenamine **IV** as yellow crystals with mp 92–93°C; published data [12]: mp 96°C.

The same product was obtained from 2-(4-chlorophenylthio)-1-nitro-1-phenylethene (**I**) under similar conditions.

(*Z*)-2-Amino-1-nitro-1,2-diphenylethene (XI) was synthesized following the above procedure with the use of a double excess of ammonia.

(*Z*)-2-Benzylamino-1-nitro-1-phenylethene (V). To a suspension of 0.15 g (5 mmol) of nitrostyrene **II** in 10 ml of dry diethyl ether we added dropwise a solution of 0.1 g (1 mmol) of benzylamine in 5 ml of dry diethyl ether. After several minutes, the mixture became homogeneous and gradually turned yellow, and a colorless solid (benzylammonium sulfinate) separated. The precipitate was filtered off, and the filtrate was kept for 25 min at 18–20°C and cooled to 0°C. Large bright yellow crystals separated and were filtered off. Yield 0.07 g. The same product was obtained from nitrostyrene **I**.

2-Diethylamino-1-nitro-1-phenylethene (VII). To a suspension of 0.15 g (0.5 mmol) of 1-nitro-1-phenyl-2-(4-tolylsulfonyl)ethene (**II**) we added dropwise a solution of 0.08 g (1 mmol) of diethylamine in 5 ml of dry diethyl ether. After 15 min, the mixture became yellow, and diethylammonium sulfinate precipitated as a colorless solid. The mixture was filtered, the filtrate was concentrated, 5 ml of anhydrous ethanol was added to the residue, the mixture was cooled to 0°C, and the yellow cubic crystals were filtered off. Yield 0.066 g.

Under analogous conditions, from nitrostyrenes **I** and **II** we obtained (*E*)-2-dipentylamino-1-nitro-1-phenylethene (**VIII**), 1-nitro-1-phenyl-2-piperidinoethene (**IX**), and (*E*)-2-morpholino-1-nitro-1-phenylethene (**X**). From nitrostyrene **II** we also synthesized 1-nitro-2-(4-nitrophenylamino)-1-phenylethene (**VI**), and from nitrostilbene **III**, 1-nitro-1,2-diphenyl-2-piperidinoethene (**XV**).

(*Z*)-2-Benzylamino-1-nitro-1,2-diphenylethene (XII). To a suspension of 0.38 g (1 mmol) of 1-nitro-1,2-diphenyl-2-(4-tolylsulfonyl)ethene (**III**) in 3 ml of methanol we added a solution of 0.22 g (2 mmol) of benzylamine in 5 ml of acetonitrile, and the mixture was heated for 20 min to 60°C until it became homogeneous. The mixture was kept for 15 min at 18–20°C and cooled to 0°C, and the precipitate of (*Z*)-nitroaminostilbene **XII** was filtered off. Yield 0.29 g, yellow crystals.

2-Dipentylamino-1-nitro-1,2-diphenylethene (**XIV**) and 2-morpholino-1-nitro-1,2-diphenylethene (**XVI**) were synthesized in a similar way. Following the above procedure (reaction time 40 min), 2-benzyl-

amino-1-nitro-1-phenylethene (**V**) was obtained from nitrostyrene **I**.

Reaction of 2-(4-chlorophenylthio)-1-nitro-1-phenylethene (I) and 1-nitro-1,2-diphenyl-2-(4-tolylsulfonyl)ethene (III) with *p*-nitroaniline. To a suspension of 0.29 g (1 mmol) of nitrostyrene **I** in 5 ml of acetonitrile we added a solution of 0.14 g (1 mmol) of *p*-nitroaniline in 5 ml of acetonitrile. The resulting suspension was heated for 4 h at 60°C (with a reflux condenser). The mixture was cooled, and the yellow precipitate of initial compound **I**, 0.35 g (95%), was filtered off.

Under analogous conditions, 98% of the initial nitrostilbene was recovered from the reaction of *p*-nitroaniline with compound **III**.

REFERENCES

1. Perekalin, V.V., Lipina, E.S., Berestovitskaya, V.M., and Efremov, D.A., *Nitroalkenes*, London: Wiley, 1994.
2. Pavlova, Z.F., Lipina, E.S, Kasem, Ya.A., and Kuz'mina, N.V., *Russ. J. Org. Chem.*, 1999, vol. 35, p. 1321.
3. Kuz'mina, N.V., Lipina, E.S., Kropotova, T.Yu., Berkova, G.A., and Pavlova, Z.F., *Russ. J. Org. Chem.*, 2001, vol. 37, p. 1259.
4. Ono, N., Kamimura, A., and Kaji, A., *J. Org. Chem.*, 1986, vol. 51, p. 2139.
5. Kamimura, A. and Ono, N., *Synthesis*, 1988, p. 921.
6. Chiara, H., Gomez-Sanchez, A., and Bellanato, J.J., *J. Chem. Soc., Perkin Trans. 2*, 1992, p. 78.
7. Fetell, A.I. and Feuer, H., *J. Org. Chem.*, 1978, vol. 43, p. 1238.
8. Gate, E.N., Meek, M.A., Schwalbe, C.H., Stevens, M.F.G., and Threadgill, M.D.. *J. Chem. Soc., Perkin Trans. 2*, 1985, p. 251.
9. Todres, Z.V., Dyusengaliev, K.I., and Kosnikov, A.Yu., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, p. 791.
10. Mukhina, E.S., Berkova, G.A., Pavlova, Z.F., Lipina, E.S., and Perekalin, V.V., *Zh. Org. Khim.*, 1990, vol. 26, p. 1447.
11. Mukhina, E.S., Pavlova, Z.F., Berkova, G.A., Lipina, E.S., and Mostyaeva, L.V., *Zh. Org. Khim.*, 1991, vol. 27, p. 910.
12. Cariou, M., *C.R. Acad. Sci., Ser. C*, 1979, vol. 289, p 255.